race, proceeded westward from its early home in the east is a fair subject for speculation. But, under any circumstances, this discovery aids in bridging over the interval between palæolithic man in Britain and in India, and adds another link to the chain of evidence by which the original cradle of the human family may eventually be identified, and tends to prove the unity of race between the inhabitants of Asia, Africa, and Europe, in Palæolithic times.

"On the Liquation of certain Alloys of Gold." By EDWARD MATTHEY, F.S.A., F.C.S., Assoc. R.S.M. Communicated by Sir G. G. STOKES, Bart., F.R.S. Received April 14,—Read May 7, 1896.

The molecular distribution of the metals in alloys of gold and of metals of the platinum group has been described by me at some length, in a series of papers which have already been published by the Royal Society.* New interest in the subject has, however, arisen in connexion with the extraordinary development in various parts of the world especially in South Africa, of certain processes which are now employed for extracting gold from its ores. Their use has been attended with the introduction into this country of a series of alloys of gold and the base metals which have hitherto rarely been met with in metallurgical industry. The base metals associated with the gold in these cases are usually the very ordinary ones lead and zinc, but their presence in the gold has given rise to unexpected difficulties, as the distribution of the precious metal in the ingots which reach this country is so peculiar, that it is not possible to estimate the value of the ingots by taking the pieces of metal required for the assay, by any of the well-known methods now in use.

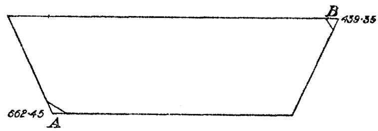
The grouping of the metal in these ingots presents much scientific as well as industrial interest, and the following is a brief statement of the facts which have been observed.

A. An ingot of gold weighing 3·545 kilograms was assayed with a view to subjecting it to the ordinary operation of refining. A piece of metal was, therefore, cut from the base of the ingot at the point marked A, and the following are the results of four assays made on this piece of metal:—

Gold	1	665·8
	2	663·6
	3	662·4
	4	658·0
Average		662·45

* 'Phil. Trans.,' A, vol. 183, p. 629, 1892. 'Roy. Soc. Proc.,' vol. 47, p. 180, 1890.

There was also 0·061 part of silver present in 1000 parts of the mass, the remainder being base alloy.



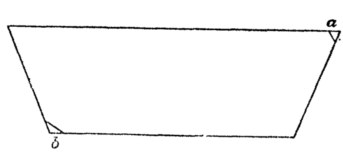
Another set of assays from the same ingot, but from the opposite end, at the point marked B, gave the following results :—

1	429·9		
2	459·5		
3	439·0		
4	429·0	Silver	0·071
Average	439·35		

The difference in the amount of gold between the two opposite ends of the ingot was, therefore, no less than 223·10 parts in 1000. The base metal present was proved by analysis to be chiefly zinc, lead, and copper, as the following results will show on metal taken by a "dip," *i.e.*, from the molten metal :—

Zinc	15·0
Lead	7·0
Copper	6·5
Iron	2·2
Nickel	2·0
Silver	7·0
Gold (by difference)	60·3
	100·0

B. Another ingot of alloyed gold weighing 12·223 kilograms gave at different parts of the ingot the following results by assay :—



Four assays on a piece of metal cut at *a*—top of ingot—

	Gold.	Silver.
1	664·0	0·090
2	662·5	0·091
3	465·0	0·076
4	661·5	0·091

Three assays at *b*—bottom of ingot—

	Gold.	Silver.
1	332·5	0·181
2	652·0	0·095
3	410·5	0·057

And seven assays were made from a "dip," viz.—

	Gold.	Silver.
1	622·0	—
2	574·4	0·072
3	653·5	0·011
4	623·2	—
5	580·0	0·138
6	603·3	—
7	562·3	—
Average of the whole number of the assays made	576·2	0·090

It became evident, therefore, that the only method of determining the true quality of this ingot consisted in actually separating the gold and silver in mass, and this was effected by dissolving in nitro-hydrochloric acid, the silver being recovered as chloride and reduced to metallic silver, and the gold precipitated by iron chloride as pure metallic gold.

The result of this operation yielded

Gold	7·504 kilograms.
Silver	0·928 ,,

which showed that the standard fineness of the ingot was

Gold	614·0
Silver	75·8

and its true value £1,028; while the value, as calculated from the average of the assays previously made,

Gold	576
Silver..........	0·090

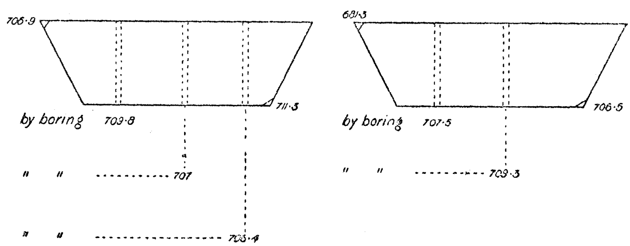
would have been only £965.

Analysis proved that the metals present other than gold were as follows :—

Silver	8·1
Lead	16·4
Zinc	9·5
Copper	4·0
Iron	0·3
Gold (by difference) . .	61·7
	100·0

The cause of the differences revealed by assays made from metal cut from various parts of the ingot was clearly due to liquation; but previous experience failed to afford any guide to the probable distribution of the precious and base metals in the ingot.

C. Another instance, and on a much larger quantity of gold alloy than the two former examples, was afforded by an ingot weighing 39·625 kilograms, which showed such great variation in its gold contents at various points that the ingot was re-melted and cast into two separate ingots, from which portions of metal were removed for assay by drilling.



All these results are the averages of assays made in *triplicate*, and a "dip" assay from the melted metal showed that it contained 701 parts of gold in 1000.

The analysis of this metal gave—

Zinc	7·1
Lead	4·9
Copper	4·8
Iron	1·4
Silver	9·2
Gold (by difference) . .	72·6
	100·0

As in the former case, the gold and silver present were isolated *in mass*, and the actual yield of fine gold and silver so obtained was as follows:—

Gold	27·914 kilograms.
Silver	3·568 „

which proved that the actual gold standard of the ingot was 703·9.

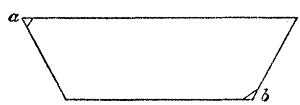
The base metal in two similar ingots was found by analysis to be composed as follows :—

	(492.)	(494.)
Silver..............	8·9	8·0
Lead	9·0	7·7
Zinc	4·8	8·5
Copper	5·2	3·2
Iron	0·4	1·6
Nickel	0·8	1·8
Gold (by difference)..	70·9	69·2
	100·0	100·0

from which it would appear that the presence of one or both of the metals—zinc and lead—bears in some degree upon these variations in quality—it being well known that gold will alloy, and be constant in quality, with either silver or copper or with both in almost any proportions.

Advancing progressively, I now cite an instance of irregular distribution in a much baser alloy of gold.

An ingot of base gold alloy (P. 13) weighing 9·570 kilograms.



Determinations from the top of this ingot gave results :—

Point *a*—

Gold.	Silver.
265·0	—
378·4	213
383·0	—

From the bottom, point *b*—

527·2	—
560·0	66
545·5	—

From a "dip" taken from the fused alloy—

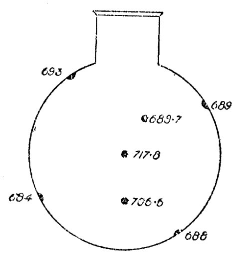
561·0	—
618·5	75
683·0	—

differences which are too significant to need comment.

In order to ascertain the effect exerted by these two metals—lead and zinc—in conjunction with gold, I prepared an alloy of 700 parts pure gold and 300 parts pure lead, and after mixing and casting into an open mould I cast the melted alloy into a spherical mould 2 in. in diameter, made of cast iron. Determinations made from different parts, after cutting the sphere into two halves, gave the following results, the assays being made in triplicate upon each portion of metal removed.

(The weight of this sphere was a little over 2 kilograms.)

FIG. 1.



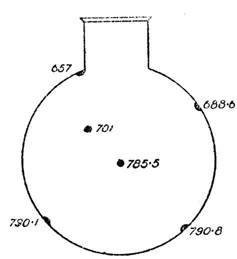
The result shows a decided tendency of the gold *to liquate to the centre of the mass.*

In the next experiment gold was alloyed with lead and zinc in the following proportions:—

Gold	75 parts.
Lead	15 „
Zinc	10 „

adding the zinc when the alloy of the first two metals was thoroughly fluid, and after casting this into an open mould, the alloy was remelted and cast into the 2-in. spherical mould before mentioned. This alloy was extremely hard and very brittle. Portions removed from the different parts of the sphere, after cutting it across, gave the following results:—

FIG. 2.



There is evidence of re-arrangement by liquation in this case which sends gold to the centre, but the result is complicated, as gravity appears also to send gold to the lower portion of the spherical mass.

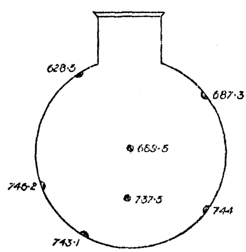
The foregoing mixture (No. 2) of

Gold	75 parts.
Lead	15 ,,
Zinc	10 ,,

was now further alloyed by the addition of 5 per cent. of pure copper and cast into a sphere which was very hard and brittle, and weighed about 2 kilograms.

The following are the results at the points shown :—

Fig. 3.



Here again, gravity appears to send gold to the lower portion of the sphere.

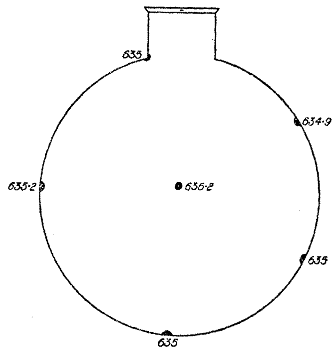
The question arises, does the silver play any part in the distribution of the baser metals, lead and zinc?

I therefore melted sphere No. 3 with 10 per cent. of silver, so that there were present :—

Gold	63·4	(by difference)
Silver........	7·8	
Copper	5·1	
Zinc	8·8	
Lead	14·5	
Iron	0·4	
	100·0	

and cast into an open mould, and subsequently into the spherical mould. The following were the results obtained of fine gold at the points indicated :—

Fig. 4.

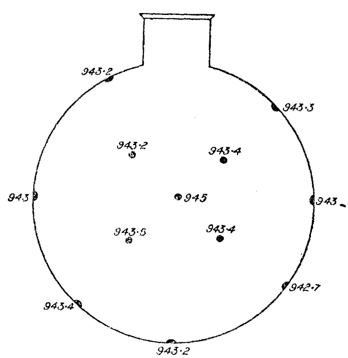


This sphere seems constant all over.

In order to see what was the effect with pure gold alloyed with metallic zinc only, I cast an alloy of fine gold with 5 per cent. of zinc into a 3-in. spherical mould. The weight of the sphere was 3·438 kilograms.

The results were as follows :—

Fig. 5.

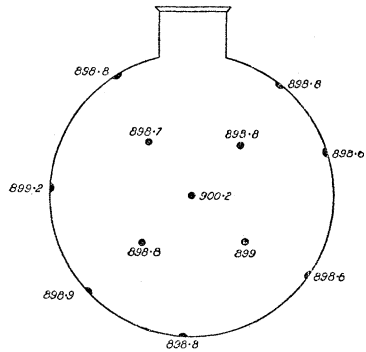


(Five per cent. zinc.

A slight but decided tendency of liquation of gold towards the centre.

The same alloy, containing 95 per cent. of gold and 5 per cent. of zinc, was then alloyed with a further 5 per cent. of zinc and cast into the same sphere. This weighed 4·218 kilograms. The results were as follows :—

FIG. 6.

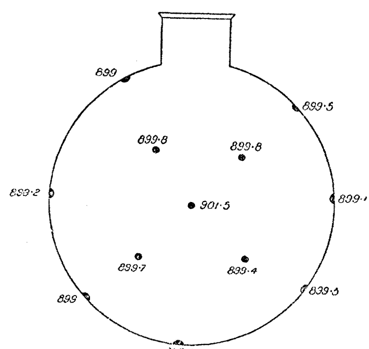


(Ten per cent. zinc.)

Feeling a little diffident about these results, I recast the foregoing alloy of gold with 10 per cent. of zinc, into the same mould.

The results were as follows :—

FIG. 7.

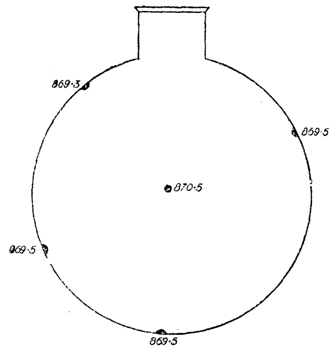


(Ten per cent. zinc.)

This shows that there is still a tendency in this gold alloy with 10 per cent. of zinc to become enriched towards the centre.

This 10 per cent. alloy was then alloyed with a further 5 per cent. of zinc and cast into the same spherical mould. The weight of this sphere was 4·021 kilograms. The results were :—

Fig. 8.



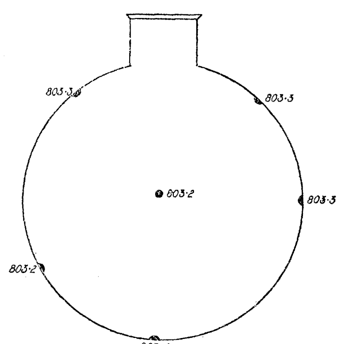
(Fifteen per cent. zinc.)

It is abundantly evident therefore, that zinc alone will not account for the differences in the ingots of impure gold; and the question arose, will the presence of a definite amount of silver in any way prevent the irregularity in composition?

To test this I alloyed the gold, which contained 15 per cent. of zinc so that it might also contain 7·5 per cent. of silver.

This was cast into the 3-in. sphere and weighed 3·934 kilograms, and assays made on portions of metal cut from it gave the following results:—

Fig. 9.



(Fifteen per cent. zinc.)

It was intended to contain—

Zinc	15·0
Silver	7·5
Gold	77·5
	100·0

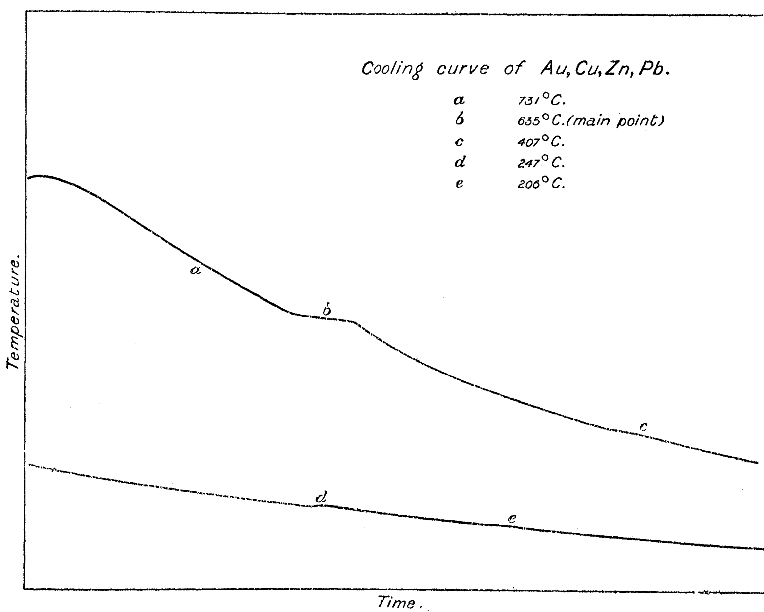
the extra richness of the gold over 77·5 being due to the volatilisation of the zinc. This experiment appears to confirm that on pp. 27, 28 (see results of fig. 4).

The foregoing experiments show that lead is far more effective as a cause of liquation than zinc, and the question arises, do zinc and lead separate into distinct layers by gravity when they are simultaneously present in a mass of gold, as they are known to do when they (lead and zinc) are melted together and allowed to solidify slowly. If they do separate, are they respectively associated with precious metal? Professor Roberts-Austen has given us a method of investigating such a problem. He has shown that it is easy to place a suitably protected thermo-junction in a mass of cooling alloy, and obtain by photography a record of the cooling of the mass,* a method which was employed by me for determining the temperatures at which the metals arsenic and antimony separate from bismuth. Applying this method to a mass weighing 44 grams of an alloy containing :—

Gold	75·0
Lead	15·0
Zinc	10·0

The following curve, No. I, is an autographic record of its solidification :—

CURVE No. I.

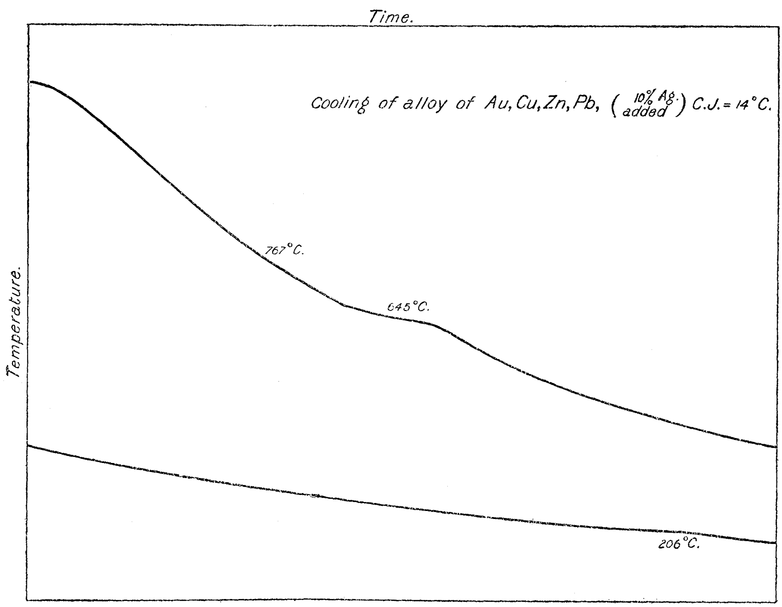


* See 'Roy. Soc. Proc.,' vol. 52, p. 467.

From this it will be evident, from the horizontal position (b) (of the curve No. I) that the mass solidifies as a whole at 635° C.; but there is a second break c in the curve at a temperature of 407° C.; and there is yet a third break at d, 247° C. These latter points evidently are connected with the solidifying points of lead and zinc, but it is probable that these metals are, in solidifying, associated with some gold.

The second curve, No. II, represents the cooling of the same mass of gold with 10 per cent. of silver added. It will be seen that the metal has still one main solidifying point b, at 645° C. The lower point (c) of the former curve is entirely absent, but there is an indication of the lead point at 206°. The results clearly indicate that silver is a solvent common to both zinc and lead, which are not, as in the previous case (Curve I) free to separate from each other. Such a mass should be fairly uniform in composition, and assays from different portions of it proved it to be so.

Curve No. II.



The latter curve (II) seems to change its direction at 767°, which is above the main solidifying point of the mass, and it remains to be seen whether this is of any significance.

The inspection of the curves so obtained at once led me to infer that silver must be a solvent for zinc and lead when these are present

in gold, and with the clear indication thus afforded I proceeded to make the following experiments:—

The alloy—

Zinc	11·0
Silver	7·5
Gold	81·5
	100·0

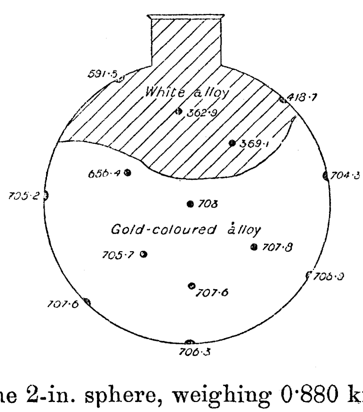
and weighing 5·680 kilograms, was now alloyed by the addition of lead to produce a similar metal to P. 13 (see p. 25), say:—

Zinc	10
Lead	20
Silver	7
Gold	63
	100

and this was cast into two spheres, a 2-in. sphere and a 3-in. sphere.

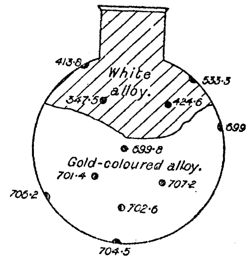
This alloy was so hard and brittle that I was compelled to cut these spheres into two by sawing them. When so cut asunder it was evident that the upper portions of both these spheres had a marked white appearance, as compared with the *lower* portions, which possessed the yellow colour of gold. The 3-in. sphere weighed 3·484 kilograms. Portions removed from these two spheres at the points indicated showed the following results:—

Fig. 10.



And those from the 2-in. sphere, weighing 0·880 kilogram —

FIG. 11.



Very marked separation takes place in both instances, the differences at various points of the sphere being very remarkable and forcibly illustrating the difficulties to which reference is made at the commencement of this paper.

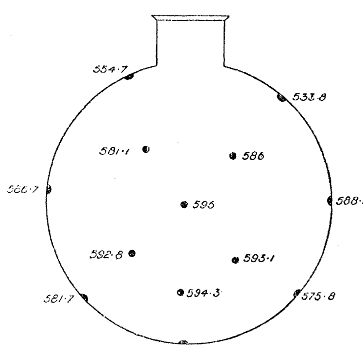
As, however, it appears, that when a certain amount of silver is present, the irregularity in composition disappears, I alloyed this mixture of—

Zinc............	10
Lead............	20
Silver	7
Gold............	63

with more silver, so that it contained 15 per cent. of silver (nearly half the united amounts of zinc and lead present in the alloy).

This, cast into the 3-in. spherical mould, showed the following results at the points indicated. In *appearance*, the metal, when sawn in two, was homogeneous. The weight of the sphere was 3·459 kilograms.

FIG. 12.



There is still evidence of liquation of gold towards the centre, but comparison of fig. 12 with those which immediately precede it will show how greatly the arrangement of the alloy has been modified by the presence of the additional 8 per cent. of silver. The proportion of silver in this alloy was proved by assay to be 15·5 per cent.

As there was still evidence of liquation, the metal was cast with still more silver, making 20 per cent. of silver in all. The alloy, when cast into a mould, proved to be almost uniform in composition, the difference between the centre and the extreme portions being very slight.

Liquation had practically ceased, a fact which proves incontestably that silver is the solvent for the base metals, zinc and lead, when they are alloyed with gold.

Conclusions.—(1) Alloys of gold with base metals, notably with lead and zinc, now largely often met with in industry, have the gold concentrated towards the centre and lower portions, which renders it impossible to ascertain their true value with even an approximation to accuracy.

(2) When silver is also present these irregularities are greatly modified.

The method of obtaining "cooling-curves" of the alloys shows that the freezing points are very different when silver is present and when it is absent from the alloy.

(3) This fact naturally leads to the belief that if the base metal present does not exceed 30 per cent., silver will dissolve it and form a uniform alloy with gold.

(4) This conclusion is sustained by the experiments illustrated by figs. 9, 10, 11, 12, which, in fact, gradually lead up to it, and enable a question of much interest to be solved.

"On the Occurrence of the Element Gallium in the Clay-Ironstone of the Cleveland District of Yorkshire. Preliminary Notice." By W. N. HARTLEY, F.R.S., Professor of Chemistry, and HUGH RAMAGE, A.R.C.S.I., F.I.C., Assistant Chemist in the Royal College of Science, Dublin. Received April 13,—Read May 7, 1896.

In the course of an investigation of flame spectra at high temperatures ('Phil. Trans.,' A, vol. 185, pp. 1029—1091 (1894)) extended to the basic Bessemer process, the authors were occupied last July and August in observing the flames from the converters at the North Eastern Steel Company's Works, at Middlesbrough-on-Tees. A large number of photographs were taken in series during the progress of the "blow," and also of the "after blow," but these will